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Zn Speciation in Combined Papermill Sludge and Acidic Mining Effluent

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Introduction: To improve the management of wastes from industrial and mining sources, alkaline papermill sludge is being considered as a liming agent to neutralize acid mine drainage. Batch adsorption experiments showed that papermill sludges (PS) were particularly efficient in removing iron, aluminum and zinc from acidic mining effluents (ME). More than 99% of iron could be removed from the ME containing 584 mg Fe L^{-1} using 5 g L^{-1} of papermill sludge. Copper, aluminum and zinc were removed at 97%, 96% and 99% from a solution containing respectively 8.09 mg Cu L^{-1}, 164 mg Al L^{-1} and 1.66 mg Zn L^{-1}. However, it is not known whether the metals actually precipitate as minerals following contact with the papermill sludge and possibly bind afterwards on the organic residues, or if they are directly adsorbed onto the organic phase. These differences in retention mechanisms may have implications for the ultimate safe disposal of the combined sludge. The objective of this study was to define the bonding mechanisms of Zn in the combined PS+ME sludge.

Methods and Materials: Samples of acidic mining effluents (pH 2.4) with original Zn concentration of 2 mg L^{-1} or spiked at 20 mg L^{-1} and 100 mg Zn L^{-1} were added to a suspension of papermill sludge (pH 8.2). The mixture was stirred for 5 min, then the pH was adjusted and maintained to 7.5 for an hour (referred hereafter as ME_2+PS, ME_{20}+PS and ME_{100}+PS, respectively). The mixtures were centrifuged and the resulting moist cake was mounted in a teflon holder behind Kapton tape for XAS analysis. A monometallic solution of 20 mg Zn L^{-1} was also combined with PS using the same procedure (Zn_{20}+PS). XAS data were collected in fluorescence mode using a 13-element detector at X-18B, National Synchrotron Light Source, Brookhaven National Laboratory, in New York.

Results: Zinc K-XANES spectra for the different combined ME+PS cakes presented few distinguishing features, although the ME_{100}+PS sample gave a unique XANES spectrum compared with samples of lower Zn concentration (Fig. 1). First shell peaks in the Zn K-EXAFS spectra (radial structure functions – RSFs) showed notable differences depending on the Zn concentration in the final ME+PS cake (Fig. 2). At the lowest Zn concentration (ME_2+PS cake), the first shell peak in the RSF was a broad doublet, indicating a combination of Zn-O and Zn-S bonding in this sample. With increasing Zn concentration (ME_{20}+PS and ME_{100}+PS), the peak shifts toward that of Zn-O bonding as indicated by comparing the spectra with those of the Zn standards (Fig. 2). Sample Zn_{20}+PS contains Zn(II) at a concentration similar to that of sample ME_{20}+PS, but in the former sample, a monometallic Zn solution was added to the ME. The RSF for this sample indicated a greater proportion of first-shell Zn-S bonding compared with ME_{20}+PS, suggesting that other metal ions such as Cu(II) in the mining effluent may compete with Zn for binding to sulfides. EXAFS fitting results of the first shell peak indicated that 46% of Zn in the Zn_{20}+PS sample was bonded to oxygen (Zn-O radial distance of 1.95 Å ± 0.02, coordination number = 1.7 ± 0.3) and 54% was bonded to sulfur (Zn-S radial distance of 2.30 Å ± 0.01; coordination number = 2.0 ± 0.1).

Conclusions: The results indicate that sulfur is a preferential ligand for Zn binding in the PS, although both XANES and EXAFS spectra showed no evidence for a well-defined ZnS mineral like our wurtzite standard. As the Zn concentration increased, the S sites apparently became saturated, and binding to oxygen (or nitrogen) ligands increased. More chalcophilic metals in the ME (e.g, Cu) may outcompete Zn for S ligands.

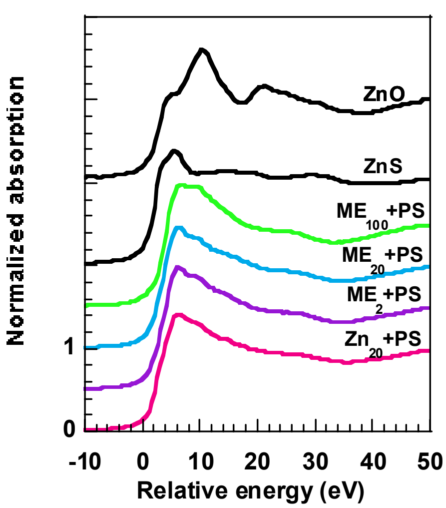

Figure 1. Zn K-XANES spectra for the combined papermill sludge and the mining effluent at 2, 20 or 100 mg Zn L^{-1}, and for the papermill sludge mixed with a monometallic Zn solution (20 mg L^{-1}).

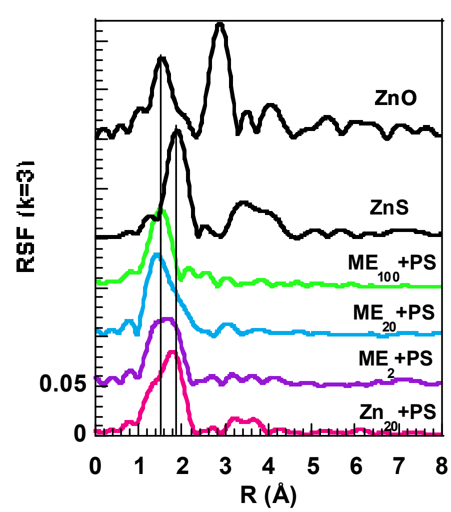

Figure 2. Zn K-EXAFS (Fourier transformed) spectra for the combined papermill sludge and the mining effluent at 2, 20 or 100 mg Zn L^{-1}, and for the papermill sludge mixed with a monometallic Zn solution (20 mg L^{-1}). Radial distances uncorrected for phase shift.